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APPLICATION NUMBER: 60/470,911

FILING DATE: May 15, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/15082

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS



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05/15/03

1c665 U.S. PTO

05-16-0360470911-05150A

PTO/SB/16 (10-01)

Approved for use through 10/31/2002. OMB 0651-0032

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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

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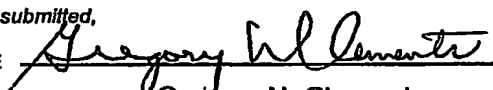
EV 332164560 US

PTO  
60/470911

INVENTOR(S)					
Given Name (first and middle [if any])	Family Name or Surname		Residence (City and either State or Foreign Country)		
Carina	Araullo-McAdams		Wilmington, North Carolina		
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
METHYL TOLUATE ESTERS					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number		Type Customer Number here		Place Customer Number Bar Code Label here	
OR					
<input checked="" type="checkbox"/> Firm or Individual Name	KoSa				
Address	4501 Charlotte Park Drive				
Address					
City	Charlotte	State	NC	ZIP	28217-1979
Country	USA	Telephone	704-586-7407	Fax	704-586-7548
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification	Number of Pages	5	<input type="checkbox"/> CD(s), Number		
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input type="checkbox"/> Other (specify)		
<input type="checkbox"/> Application Data Sheet	See 37 CFR 1.76				
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/>	Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)
<input type="checkbox"/>	A check or money order is enclosed to cover the filing fees				
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<input checked="" type="checkbox"/>	Payment by credit card. Form PTO-2038 is attached.				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/>	No.				
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Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME

Gregory N. Clements

TELEPHONE

704-366-6642

Date

05/15/2003

REGISTRATION NO.

(if appropriate)

Docket Number:

30,713

P2003/01

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This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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**FEE TRANSMITTAL**  
**for FY 2003**

Effective 01/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$ 160.00)**Complete if Known**

Application Number	
Filing Date	
First Named Inventor	Carina Araullo-McAdams
Examiner Name	
Art Unit	
Attorney Docket No.	P2003-01

**METHOD OF PAYMENT (check all that apply)**☐ Check ☒ Credit card ☐ Money Order ☐ Other ☐ None☒ Deposit Account:

Deposit Account Number	04-1448
Deposit Account Name	Dougherty & Clements LLP

The Commissioner is authorized to: (check all that apply)

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☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.
**FEE CALCULATION****1. BASIC FILING FEE**

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1001	750	2001	375	Utility filing fee	
1002	330	2002	165	Design filing fee	
1003	520	2003	260	Plant filing fee	
1004	750	2004	375	Reissue filing fee	
1005	160	2005	80	Provisional filing fee	160.00
<b>SUBTOTAL (1)</b>					<b>(\$ 160.00)</b>

**2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE**

Total Claims		-20** =		X		=	
Independent Claims		-3** =		X		=	
Multiple Dependent						=	

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1202	18	2202	9	Claims in excess of 20	
1201	84	2201	42	Independent claims in excess of 3	
1203	280	2203	140	Multiple dependent claim, if not paid	
1204	84	2204	42	** Reissue independent claims over original patent	
1205	18	2205	9	** Reissue claims in excess of 20 and over original patent	

**SUBTOTAL (2)** (\$ 0.00)

\*\*or number previously paid, if greater; For Reissues, see above

**3. ADDITIONAL FEES**

Large Entity Small Entity

Fee Code	Fee (\$)	Fee Code	Fee (\$)	Fee Description	Fee Paid
1051	130	2051	65	Surcharge - late filing fee or oath	
1052	50	2052	25	Surcharge - late provisional filing fee or cover sheet	
1053	130	1053	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for <i>ex parte</i> reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	410	2252	205	Extension for reply within second month	
1253	930	2253	465	Extension for reply within third month	
1254	1,450	2254	725	Extension for reply within fourth month	
1255	1,970	2255	985	Extension for reply within fifth month	
1401	320	2401	160	Notice of Appeal	
1402	320	2402	160	Filing a brief in support of an appeal	
1403	280	2403	140	Request for oral hearing	
1451	1,510	1451	1,510	Petition to institute a public use proceeding	
1452	110	2452	55	Petition to revive - unavoidable	
1453	1,300	2453	650	Petition to revive - unintentional	
1501	1,300	2501	650	Utility issue fee (or reissue)	
1502	470	2502	235	Design issue fee	
1503	630	2503	315	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee under 37 CFR 1.17(q)	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	750	2809	375	Filing a submission after final rejection (37 CFR 1.129(a))	
1810	750	2810	375	For each additional invention to be examined (37 CFR 1.129(b))	
1801	750	2801	375	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

Other fee (specify) \_\_\_\_\_

\*Reduced by Basic Filing Fee Paid

**SUBTOTAL (3)** (\$ 0.00)**SUBMITTED BY**

Name (Print/Type)	Gregory N. Clements	Registration No. (Attorney/Agent)	30,713	Telephone	704-366-6642
Signature	<i>Gregory N. Clements</i>	Date	5/15/2003		

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I, Margaret Hieb, do hereby certify that the foregoing or attached documents are being deposited with the United States Postal Service as Express Mail, postage prepaid, in an envelope addresses to: Commissioner of Patents and Trademarks, Washington, D.C. 20231 on May 15, 2003.

Margaret Hieb  
Name: Margaret Hieb

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May 15, 2003  
Date of Deposit

EV332164560US

## PATENT

## SPECIFICATION

INVENTOR: CARINA ARAULLO-MCADAMS

TITLE: METHYL TOLUATE ESTERS

Background of the Invention

## 1) Field of the Invention

This invention relates to liquid ester compositions and their use as plasticizers, and diluents in binder formulations. More particularly, this invention relates to the mono- or di-ester of methyl toluic acid with a diol containing 2 to 6 carbon atoms that are low viscosity liquids at 20° C.

## 2) Description of Prior Art

Esters derived from benzoic, substituted benzoic and toluic acid with aliphatic alcohols, and the methods for preparation, have been described in the prior art. These esters are primarily used as plasticizers for polymers to facilitate processing and increase flexibility and toughness. Polyvinyl chloride homo- and co-polymers (PVC) account for the majority of the plasticizer usage. The most common plasticizer, dioctyl phthalate (DOP), has been the subject of environmental and toxicological studies and is a high cost additive. Benzoate plasticizers (dipropylene glycol dibenzoate, diethylene glycol dibenzoate) have been introduced as plasticizers but only have moderate compatibility with PVC.

US Patent 2,585,448 to Emerson et al. discloses mixtures of esters prepared by esterifying diols such as diethylene glycol, triethylene glycol with aromatic monocarboxylic acids such as benzoic acid and alkyl substituted benzoic acid.

US Patent 4,656,214 to Wickson discloses diesters 1) linear glycols containing from 2 to 8 carbon atoms, 2) a first carboxylic acid of the formula  $R^1R^2R^3C(O)OH$  and 3) a second carboxylic acid of the formula  $R^5C(O)OH$ , wherein  $R^1$  and  $R^2$  are individually selected from alkyl containing from 1 to 4 carbon atoms,  $R^3$  is hydrogen or alkyl from 1 to 6 carbon atoms,  $R^5$  is selected from the group consisting of phenyl, mono- di- and trialkyl-substituted phenyl containing from 9 to 12 carbon atoms and  $-(CH_2)_nPh$  where Ph is phenyl and the value of n is from 1 to 6, inclusive. The esters contain from 16 to 19 carbon atoms and are useful as stain-resistant plasticizers for polyvinyl chloride.

US Patent 5,990,214 to Arendt et al. discloses liquid compositions of mixtures of esters derived from diethylene and triethylene glycol and benzoic or toluic acid. These esters are useful as plasticizers for PVC.

WO 02/083621 to Lang et al. discloses mixed esters prepared in a single step reaction from diols such as diethylene glycol, benzoic acid and an aliphatic acid such as lauric acid. These are liquid at room temperatures and are useful as plasticizers for PVC.

These ester compositions are still slightly volatile, and there is a need for ester compositions with lower volatility than commonly used materials such as dibutyl ester.

Phenolic resins, including furan resins and phenolic urethanes, are used as binders for building products, wood products, insulation, foundry materials, abrasives and friction materials. In these formulations hydrocarbon solvents are used as diluents to reduce the viscosity of the phenolic resins. There is a need for diluents that have low volatility, or that can be incorporated into the resin, in order to reduce the VOC level. There is a need for diluents which produce low smoke in foundry applications.

There is also a need for diluents and solvents that reduce the VOC level in other formulations such as paints, inks, elastomers, adhesives, etc.

There is also a need for low viscosity dye carriers for textiles, polyurethanes, and paper applications which are more economical than existing carriers.

### **Summary of the Invention**

The present invention is based on the discovery that diethylene glycol esters or triethylene glycol esters of toluic acid, prepared from the methyl-p-toluate produced in a Witten dimethyl terephthalate process, have low volatility and have low melting points. In addition to being used as plasticizers, they also can act as diluents or reactants to reduce viscosity in foundry binders, casting resins and polyurethane applications.

### **Detailed Description of the Invention**

Methyl-p-Toluate (MpT) can be transesterified, using conventional catalysts, with diols to form the mono- or di-ester. A common diol is diethylene glycol or triethylene glycol, but the pure toluate esters have high melting points.

In the Witten process p-xylene is converted through oxidation and esterification with methanol to DMT. After the first oxidation process a stream that is rich in MpT is produced that is normally recycled for further oxidation. Surprisingly it has been found that this stream can be esterified with diols to produce toluic esters that are liquid at room temperature and have low volatility.

The preferred ester is either the mono- or di-diethylene glycolate. The di-ester can be used as a plasticizer or diluent, and the mono-ester can be reacted into the phenolic resin or urethane.

This compound is also useful as a diluent in binder applications which use hydrocarbon solvents. In order to improve the compatibility of these esters with systems that contain hydrocarbon solvents, soybean oil, or other vegetable oils, or tall oil fatty acids may be reacted into the esters.

### Examples

The process stream used as the source of MpT had the composition (weight %) set forth in Table 1. This data represents the range of average monthly composition of the components over a 5-year period.

Table 1

Compound	Low value	High Value
Methyl-p-toluate	68	84
Dimethyl terephthalate	6	20
Methyl-p-formyl benzoate	2	6
p-toluic acid	1	5
Methyl benzoate	1	3
Others		

### Example 1

500 g of process stream 150 g of diethylene glycol (DEG) were heated with 0.04 wt % Tyzor catalyst in a reactor. The reactor was stirred and was equipped with a water-cooled reflux condenser. The contents of the reactor were rapidly heated to 180° C, and then gradually heated to 220° C over a 3 hour period. After cooling, the product had an acid number of 0.35 and a viscosity of 245.

### Example 2

The process of Example 1 was repeated with a reactor charge of 400 g process stream, 180 g DEG, 100 g tall oil fatty acid, and 0.27 g Tyzor. The temperature was raised up to 240° C. The product had an acid number of 3.91 and a viscosity of 305.

### Example 3

The process of Example 1 was repeated with a reactor charge of 300 g process stream, 150 g DEG and 0.18 g Tyzor. When the temperature reached 220° C, 1 hour, 100

g soybean oil was added and the reaction mixture held at 220° C for 2 hours. The product had an acid number of 1.1 and a viscosity of 66.

#### **Example 4**

Example 3 was repeated with the replacement of the DEG with 100 g triethylene glycol. The product had a viscosity of 41.

#### **Example 5**

Example 3 was repeated with the replacement of the DEG with ethylene glycol. The product had a viscosity of 97.

These esters can be used to replace the typical solvents used in binder compositions. US 4,615,372 describes a typical phenolic resin binder that contains 45-50 wt. % solvents, usually a mixture of aromatic hydrocarbons and moderately polar solvents. US 4,293,480 discloses a foundry binder based on a polyol, an isocyanate urethane polymer and a urethane catalyst. Again a polar solvent is used in this composition and can be replaced by the toluate esters of this invention.

Thus it is apparent that there has been provided, in accordance with the invention, a low viscosity, low volatility, and low melting point ester useful as a plasticizers for PVC or as a solvent in binder compositions, that fully satisfies the objects, aims and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the spirit and broad scope of the invention.



What is claimed is:

- 1) A low viscosity, low volatility, and low melting point ester useful as a plasticizers for PVC or as a solvent in binder compositions, comprising a mono- or diester prepared from the reaction of toluic acid or its ester, with diethylene or triethylene glycol.
- 2) The ester of claim 1, said ester is a low viscosity liquid at 20° C.
- 3) A method of making a low viscosity, low volatility, and low melting point ester by reacting methyl-p-toluate with diethylene or triethylene glycol.
- 4) The method of claim 3, wherein said preparation of said ester is from a MpT rich stream from a Witten DMT process.